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CONDENSATE TREATMENT PROCESS AND HOLLOW FIBER MEMBRANE MODULE FOR CONDENSATE TREATMENT

[FUKUSUI NO SHORI HOUHOU OYOBI FUKUSUI SHORI YOU CHUUKUUSHIMAKU MOJUURU]

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Specification

[Claims]

[Claim 1]

A process for aqueous condensate treatment with the help of a hollow fiber membrane module comprising a hollow fiber membrane, wherein a composite microporous hollow fiber membrane produced by laminating three or more three-dimensional membranes made of polyolefin having a plurality of micropores formed by stacked lamellae and microfibrils joined to said stacked lamellae, in which the innermost layer and outermost layer serve as support layers and the intermediate layer sandwiched therebetween is a dense layer in which the average pore diameter of the micropores is smaller than the average pore diameter of the micropores of the support layers, is used as the above-mentioned hollow fiber membrane.

[Claim 2]

The process for aqueous condensate treatment according to claim 1, wherein the above-mentioned support layers are thicker than the dense layer, the thickness of a single support layer is 20-50 μm, and the porosity of the entire above-mentioned hollow fiber membrane is 75 vol% or more.

[Claim 3]

The process for aqueous condensate treatment according to claim 1 or claim 2, wherein the above-mentioned hollow fiber membrane is coated with a hydrophilic polymer and its microfibrils are gathered into bundles of multiple microfibrils each.

[Claim 4]

The process for aqueous condensate treatment according to any one of claims 1 through 3, wherein the rate of coating with the above-mentioned hydrophilic polymer is from 3 wt% to 30 wt% based on the hollow fiber membrane prior to coating and the ratio Db/Da of the average distance Db between the microfibril bundles of the support layers to the average distance Da between the microfibril bundles of the dense layer after coating is in the range of 1.3 to 4.0.

[Claim 5]

A hollow fiber membrane module for aqueous condensate treatment comprising a hollow fiber membrane, wherein the above-mentioned hollow fiber membrane is produced by laminating three or more three-dimensional membranes made of polyolefin having a plurality of micropores formed by stacked lamellae and microfibrils joined to said stacked lamellae, in which the innermost layer and outermost layer serve as support layers and the intermediate layer sandwiched therebetween is a dense layer, in which the average pore diameter of the micropores is smaller than the average pore diameter of the micropores of the support layers.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a process for aqueous condensate treatment generated by nuclear power plants, thermal power plants, etc., as well as to a hollow fiber membrane module for the treatment of such aqueous condensate.

[0002]

[Prior Art]

In the past, precoated filters made of ion exchange resin have been used for the purification treatment of aqueous condensates generated by nuclear power plants, thermal power plants, etc. However, the problem with precoated filters made of ion exchange resin is their short life, and especially, the fact that after treating a radioactivity-laden aqueous condensate generated at a nuclear power plant, the precoated filters have to be stuffed in drums and stored away. For this reason, as a recent development in the treatment of aqueous condensates, microporous hollow fiber membranes made of polyolefin have come to be used as membrane materials that possess useful characteristics such long life, incineratability after aqueous condensate filtration treatment, and the ability to minimize the generation of secondary wastes.

[0003]

As a representative example of the hollow fiber membranes used in the hollow fiber membrane modules employed in the treatment of aqueous condensates, Japanese Unexamined Patent Application Pub. No. Sho 57[1982]-066114 discloses a composite hollow fiber membrane made of polyethylene, in which slit-like micropores formed by nodes formed between microfibrils oriented along the longitudinal axis of the hollow fiber membrane and stacked lamellae oriented in the membrane thickness direction of the hollow fiber membrane are stacked in layers within the membrane walls of the hollow fiber membrane and penetrate therethrough from one surface of the membrane toward the other surface, thereby forming a uniform microporous structure in the thickness direction.

[0004]

This hollow fiber membrane is manufactured by melt-forming polyethylene and then stretching the formed product. Namely, a microporous membrane of the specific structure described above is formed by forming lamellar layered crystals (stacked lamellae) within the membrane walls of the formed product by forming polyethylene under specific spinning conditions and then subjecting it to annealing treatment, followed by delaminating the stacked lamellae by stretching the formed product while at the same time growing fibrils interconnecting the lamellar layered crystals. Due to the specific microporous structure described above, this membrane has excellent mechanical strength. Furthermore, as another characteristic of the membrane, there is little danger that impurities from the membrane will get into the purified water because no solvents are used in the manufacturing process.

[0005]

[Problems to be Solved by the Invention]

However, hollow fiber membranes made of polyolefin are hydrophobic membranes and, as a result, when such hollow fiber membranes are used in the treatment of aqueous condensates, they have to be subjected to hydrophilic treatment with alcohol. Hollow fiber membranes produced by coating a hollow fiber membrane made of polyolefin with an ethylene-polyvinyl alcohol copolymer or hollow fiber membranes manufactured from a polyolefin resin blended with an ethylene-polyvinyl alcohol copolymer are known to reduce such difficulties (see Japanese Examined Patent Application Pub. No. Hei 6[1994]-096102). However, despite the fact that the time-dependent decrease in the volume of aqueous permeate due to micropore collapse and clogging can be prevented in such hollow fiber membranes, there have been no improvements in terms of increasing the inherently low aqueous permeate production that is characteristic of these microporous hollow fiber membranes. For this reason, the problem with aqueous condensate treatment processes relying on such hollow fiber membranes is that while there little time-dependent variation in the volume of treated water, the volume of treated water cannot be increased.

[0006]

In order to increase the volume of aqueous permeate per hollow fiber membrane module, one may increase the number of installed hollow fiber membranes or increase the length of the hollow fiber membranes. However, while the volume of aqueous permeate did increase in proportion to the number of installed membranes to a certain degree when the density of installation of the hollow fiber membranes was increased, as soon as the density of placement exceeded a certain level, resistance to the passage of the aqueous condensate into the central portion of the hollow fiber membrane bundle increased, as a result of which the volume of aqueous permeate could no longer be increased in proportion to the number of installed membranes. Further, when the surface area was increased by increasing the length of the hollow fiber membranes, up to a certain length, the volume of aqueous permeate increased, but due to the relationship between the inner diameter of the hollow fiber membranes and the performance of the membranes, above a certain length, the resistance of the flow channels inside the hollow fiber membranes became a rate-limiting factor and the volume of aqueous permeate could not be increased in proportion to the length.

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[0007]

Although processes, in which membranes of large micropore sizes are selected from among the hollow fiber membranes mentioned above, have been considered as another type of processes capable of increasing the volume of aqueous permeate, purified water of the desired water quality is not obtained because the fractionating performance of the hollow fiber membranes becomes insufficient. Further, while the volume of aqueous permeate did increase when using thin hollow fiber membranes, in that case, the mechanical strength of the microporous hollow fiber membranes tended to be insufficient and aqueous condensates could not be treated in a stable manner for an extended period of time. For this reason, there was the problem that many large hollow fiber membrane modules had to be used and a considerable amount of process space was required for the treatment of a large volume of aqueous condensate.

[0008]

Thus, it is assumed that the treatment of aqueous condensates produced by nuclear power plants, thermal power plants, and the like would require a treatment process that is capable of treating large volumes of water, provides excellent aqueous condensate purification performance with little time-dependent variation in the volume of treated water, and enables stable treatment for an extended period of time and in a small footprint. In addition, such a treatment process requires hollow fiber membranes that offer a high level of water permeation performance (flux) and a high level of fractionating performance that allows for cladding particle removal, are not prone to clogging or sustaining cladding-induced damage, exhibit little increase in differential pressure during filtration, and possess a mechanical strength (durability) that is sufficient for miniaturization, achieving an increased useful life, backflushing, bubbling, chemical cleaning, etc.

[0009]

Thus, Japanese Unexamined Patent Application Pub. No. Hei 9[1997]-108671 discloses a process for aqueous condensate treatment utilizing two-layer microporous hollow fiber membranes made of polyolefin that are produced by bonding a microporous hollow fiber membrane having micropores capable of separating particles of a predetermined particle size to another microporous hollow fiber membrane having micropores that are larger than the above-mentioned micropores at a certain ratio. The microporous hollow fiber membranes used in this treatment process were composite membranes made up of a small-pore dense layer, which was responsible for its fractionating performance (internal layer), and large-pore functional reinforcing layers, which served a reinforcing function, produced a large volume of aqueous permeate, and were resistant to clogging (external layers). In comparison with the conventional hollow fiber membranes (homogeneous membranes) of the same fractionating performance, these membranes retained enough fractionating performance for cladding removal while exhibiting excellent resistance to clogging, increased useful life, and high water permeation performance, as well as making the cartridges more compact by reducing the surface area of the membrane.

[0010]

However, while the aqueous condensate treatment process that made use of these microporous hollow fiber membranes did provide excellent aqueous condensate purification performance, exhibited little time-dependent variation in the volume of treated water, and permitted treatment in a stable manner for an extended period of time, the volume of treated water it provided was still insufficient and the process required a large amount of process space. For this reason, there is a desire to achieve increased aqueous permeate volumes and compactness by further improving the water permeation performance (flux) of the hollow fiber membranes while maintaining the above-described performance of the hollow fiber membranes used for aqueous condensate treatment.

[0011]

Thus, it is an object of the present invention to provide an aqueous condensate treatment process that is capable of treating large volumes of water, provides excellent aqueous condensate purification performance with little time-dependent variation in the volume of treated water, and enables stable operation for an extended period of time and in a small footprint. Further, another object is to provide a process for aqueous condensate treatment, in which the amount of wastes generated after aqueous condensate treatment can be minimized. Further, yet another object is to provide a hollow fiber membrane module for aqueous condensate treatment that offers high water permeation performance and fractionating performance, is resistant to clogging, and has excellent mechanical strength and durability.

[0012]

[Means for Solving the Problems]

In order to solve the above-mentioned problems, the present inventors have been painstakingly developing microporous hollow fiber membranes for a high-performance hollow fiber membrane module suitable for the treatment of aqueous condensates and, as a result, arrived at the present invention by discovering that a compound microporous hollow fiber membrane that exhibits little decrease in the volume of aqueous permeate produced by the membrane regardless of the increased membrane thickness is obtained by forming a composite microporous hollow fiber membrane, in which a microporous membrane (dense layer) having micropores capable of separating particles of a predetermined particle size is joined to other microporous membranes (support layers) having micropores that are larger than the above-mentioned micropores at a certain .

ratio, and that adopting a three-layer structure wherein, in terms of the position of the dense layer responsible for fractionating performance inside the composite porous hollow fiber membrane, the dense layer is sandwiched in between the support layers, i.e. the dense layer is positioned as an intermediate layer, makes it possible to manufacture a hollow fiber membrane module that maintains excellent performance in terms of clogging resistance while producing larger volumes of aqueous permeate than composite hollow fiber membranes with dense internal layers or, quite naturally, conventional homogeneous membranes.

[0013]

In other words, the inventive process for aqueous condensate treatment is a process for treating aqueous condensate with the help of a hollow fiber membrane module comprising hollow fiber membranes, wherein the above-mentioned hollow fiber membranes are composite microporous hollow fiber membranes produced by laminating three or more three-dimensional membranes made of polyolefin having a plurality of micropores formed by stacked lamellae and microfibrils joined to said stacked lamellae, in which the innermost layer and outermost layer serve as support layers and the intermediate layer sandwiched therebetween is a dense layer in which the average pore diameter of the micropores is smaller than the average pore diameter of the micropores of the support layers.

[0014]

Further, the above-mentioned support layers are preferably thicker than the dense layer, the thickness of a single support layer is in the range of from 20 to 50 μm, and the porosity of the entire above-mentioned hollow fiber membrane is 75 vol% or higher. Further, the above-mentioned hollow fiber membranes are preferably coated with a hydrophilic polymer and the microfibrils are gathered into bundles of multiple microfibrils each. Further, the rate of coating with the above-mentioned hydrophilic polymer is from 3 wt% to 30 wt% based on the hollow fiber membrane prior to coating and the ratio Db/Da of the average distance Db between the microfibril bundles of the support layers to the average distance Da between the microfibril bundles of the dense layer after coating is in the range of 1.3 to 4.0. Further, the inventive hollow fiber membrane module for aqueous condensate treatment is a hollow fiber membrane module for aqueous condensate treatment comprising hollow fiber membranes, wherein the above-mentioned hollow fiber membranes are produced by laminating three or more three-dimensional films made of polyolefin having a plurality of micropores formed by stacked lamellae and microfibrils joined to said stacked lamellae, in which the innermost layer and outermost layer serve as support layers and the intermediate layer sandwiched therebetween is a dense layer in which the average pore diameter of the micropores is smaller than the average pore diameter of the micropores of the support layers.

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[0015]

[Embodiments of the Invention]

The hollow fiber membrane module employed in the inventive aqueous condensate treatment process comprises hollow fiber membranes used as filtration membranes. Thus, for example, a representative configuration is obtained by securing both end portions of hollow fiber membranes assembled in the shape of the letter "U" to water collector units with the help of a potting agent. However, many other configurations may be used as well.

[0016]

FIG. 1 is a schematic cross-sectional view illustrating an exemplary hollow fiber membrane module used in the inventive aqueous condensate treatment process. The structural member 1, which is tubular in shape, has openings 1b and 1b, which open vertically in the figure.

The composite microporous hollow fiber membrane 3 (hereinafter referred to as the "hollow fiber membrane 3" for short) is folded in the shape of the letter "U", with its end portions 3a inserted through one of the openings 1b of the structural member 1, secured by an anchor member 2, which is located inside the structural member 1, and thus attached to the structural member 1. The end portions 3a of this hollow fiber membrane 3 are kept open, with a collection surface 1a formed by these end portions 3a and the above-mentioned anchor member 2.

[0017]

In addition to tubular members, members having a rectangular cross-section taken in a direction parallel to the surface of the openings may be used as the structural member 1. There are no limitations as to its shape. Further, its outer surface can be of different shapes depending on the shape of the shape of the location of installation of the hollow fiber membrane module. The anchor member 2 is usually formed by curing epoxy resin, unsaturated polyester resin, polyurethane and other liquid resins. The hollow fiber membrane 3 can be attached to the structural member 1 with one of its ends sealed and arranged in linear fashion and the other end portion kept open.

[0018]

When OUT→IN filtration is carried out in this hollow fiber membrane module, the liquid to be treated permeates through the surface of hollow fiber membrane 3 into the hollow fiber membrane 3. The liquid then moves through the hollow fiber membrane 3 and filtrate is discharged from the open end portion 3a, which constitutes the collection surface 1a. At such time, the liquid to be treated supplied to the surface of the hollow fiber membrane 3 and the filtrate discharged from the end portion 3a are separated in a fluid-tight manner by the anchor member 2. When IN→OUT filtration is performed, the liquid to be treated is supplied to collection surface 1a. From the end portion 3a, which constitutes this collection surface 1a, the liquid to be treated enters the hollow fiber membrane 3 and permeates through the hollow fiber membrane 3, with the filtrate discharged.

[0019]

The composite microporous hollow fiber membrane (referred to as the "hollow fiber membrane" for short below) used in the inventive aqueous condensate treatment process, which is produced by laminating three or more three-dimensional membranes having a plurality of micropores formed by stacked lamellae and microfibrils joined to said stacked lamellae, comprises a dense layer and support layers, in which the average pore diameter of the micropores is larger than that of the above-mentioned dense layer. The above-mentioned dense layer and the above-mentioned support layers are formed with a large number of micropores produced as a result of stretching a spun unstretched hollow fiber membrane. Namely, subjecting a melt-spun unstretched membrane to stretching treatment causes stress to accumulate in structurally weak non-crystalline portions, chains are selectively elongated in the direction of stretching, cracks develop between the stacked lamellae, and, at the same time, part of the stacked lamellae undergo delamination, resulting in the formation of microfibrils. In addition, those portions of the stacked lamellae that have high cohesive strength withstand the stress while maintaining their structure and, as shown in FIG. 2, slit-like micropores 22, 22, … are formed between the many microfibrils 20, 20, … aligned in the direction of stretching and the stacked lamellae 18, 18, …, to which they are joined.

[0020]

The pore diameter, i.e. the size, of the micropores 22 is expressed by two parameters, that is, the average value of the length L of the microfibrils 20 (corresponding to the length of the long side of the slit-like micropores 22 or the distance between the stacked lamellae 18) and the average value of the microfibril spacing W. In the process of filtration using the hollow fiber membrane, the volume of aqueous permeate depends mainly on the length L of the microfibrils, such that the longer the microfibrils 20, the larger the volume of aqueous permeate. On the other hand, the fractionating performance of the membrane depends mainly on the distance between the microfibrils W, such that the narrower the microfibril spacing W, the higher the fractionating performance can be.

[0021]

In this hollow fiber membrane, its fractionating performance is enhanced by the dense layer, which has relatively smaller micropores. In addition, the strength of the membrane is enhanced and the volume of aqueous permeate is increased by the support layers, which have relatively larger micropores. As a result, a high permeation flow rate, high fractionating performance, and high durability are obtained in a hollow fiber membrane module utilizing this hollow fiber membrane.

[0022]

In the dense layer, the average microfibril length is preferalby 0.2-5 μm and the average microfibril spacing is preferably 0.02-0.3 μm. When the microfibril length is smaller than 0.2 μm or when the microfibril spacing is smaller than 0.02 μm, the filtration resistance of the dense layer increases and the volume of aqueous permeate produced by the entire hollow fiber membrane decreases. Further, when the microfibril length is longer than five μm, the mechanical strength of the dense layer tends to be insufficient. Further, when the microfibril spacing is wider than 0.3 μm, the fractionating performance of the hollow fiber membrane tends to decrease. In the support layers, the average microfibril length is preferalby 0.5-10 μm and the average microfibril spacing is preferably 0.1-0.6 μm. When the microfibril length is smaller than 0.5 μm or when the microfibril spacing is smaller than 0.1 μm, the volume of aqueous permeate produced by the entire hollow fiber membrane is insufficient. Further, when the microfibril length is longer than 10 μm, the elongation at break of the hollow fiber membrane after stretching tends to be insufficient. Further, when the microfibril spacing is wider than 0.6 μm, the mechanical strength tends to be insufficient as well.

[0023]

Further, since the liquid to be treated is supplied from the support layers with relatively large micropores to the dense layer with relatively small micropores, the hollow fiber membrane is less susceptible to clogging. OUT→IN filtration, in which the liquid to be treated is supplied from the surface of the hollow fiber membrane, is usually more efficient. Therefore, when the support layers serve as the outermost layers and the dense layer is disposed on the inside, the support layers are disposed in the feed side of the liquid to be treated. This is desirable because the membrane is rendered more resistant to clogging.

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[0024]

On the other hand, the rate-limiting factor of the volume of aqueous permeate produced by the hollow fiber membrane is the dense layer, which has smaller micropores. Therefore, it is desirable to make the surface area of the dense layer as large as possible in order to increase the volume of aqueous permeate. Therefore, it is desirable to enlarge the surface area of the dense layer by disposing it as close as possible to the external layer side rather than to the internal layer side of the hollow fiber membrane to make its inner diameter and outer diameter larger. Further, when the hollow fiber membrane is manufactured, due to the heat insulating effects of the hollow fiber membrane itself, the internal layer side tends to be insufficiently cooled. For this reason, the polymer molecule chains tend to crystallize without undergoing sufficient elongation stress (stress proportional to viscosity). It is believed that when there is a disordered crystal orientation, the stretching treatment results in non-uniform micropore dimensions (especially, microfibril spacing) in the thickness direction after stretching and the fractionating performance of the dense layer decreases. In order to prevent such a fractionating performance degradation, it is desirable to dispose the dense layer as close to the external layer side as possible so as to allow it to be sufficiently cooled.

[0025]

Therefore, in the present invention, the hollow fiber membrane preferably has a structure composed of three or more layers, in which support layers are disposed in the innermost and outermost layers, while the dense layer is disposed therebetween as an intermediate layer. Further, since in this case the innermost and outermost layers are support layers, the membrane is not prone to clogging regardless of whether the liquid to be treated is supplied from the outside or inside of the hollow fiber membrane. In addition, due to the fact that the dense layer, which serves as a separation layer, is sandwiched between the support layers as an intermediate layer, the support layers protect the dense layer from external damage during handling and filtration.

[0026]

Further, the hollow fiber membrane used in the inventive aqueous condensate treatment process is preferably coated with a hydrophilic polymer to make it readily wettable. Namely, the surface of the microfibrils and nodes of the stacked lamellae of the hollow fiber membrane are coated with a hydrophilic polymer. As shown in FIG. 3, when such hydrophilic treatment is carried out, the microfibrils are gathered into microfibril bundles 21 of multiple microfibrils each, the micropores 22 change their shape from a slit-like shape to an oval shape, and the average pore diameter of the micropores 22 can be increased.

[0027]

In this hydrophilized hollow fiber membrane, the size of the micropores 22 of the dense layer is represented by the average distance between the microfibril bundles 21 (average pore diameter) Da. In addition, the Da is preferably 0.2 to 0.5 μm, and even more preferably, 0.3 to 0.4 μm. A hollow fiber membrane, in which the above-mentioned Da is 0.2 μm or more, produces a particularly significant volume of aqueous permeate, and a hollow fiber membrane having an excellent microparticle-impeding ability and exhibiting high frationating performance can be obtained if the Da is 0.5 μm or less.

[0028]

In the hydrophilized hollow fiber membrane, the size of the micropores 22 of the support layers, i.e. the average distance between the micropore bundles 21 shown in FIG. 3 (average pore diameter) Db is 0.2 to 1 μm or, preferably, 0.4 to 0.5 μm. In a hollow fiber membrane having support layers whose Db is less than 0.2 μm, the rate of water permeation decreases, while the membrane strength of the hollow fiber membrane decreases when the Db exceeds 1 μm.

[0029]

Further, the ratio of Db to Da is preferably $1.3 \leq Db/Da \leq 4.0$. If the ratio of Db/Da is less than 1.3, a hollow fiber membrane exhibiting high fractionating performance and producing large volumes of aqueous permeate may not be obtained. If the ratio of Db/Da exceeds 4.0, there are more differences in the physical properties of the material of the dense layer and the material of the support layers, as a result of which stability during melt-spinning or stretching treatment decreases. Further, the average distance Mb between the nodes of the stacked lamellae 18 in the dense layer is preferably 0.4 to 4.0 μm or, even more preferably, 0.7 to 2.0 μm. If the Mb is less than 0.4 μm, the rate of water permeation decreases, and the membrane strength of the hollow fiber membrane decreases if the Mb exceeds 4.0 μm.

[0030]

Incidentally, the above-mentioned average distances between microfibril bundles Da, Db are measured in the following manner. Namely, samples are prepared by cutting extremely thin slices from the hollow fiber membrane along the axial direction of the fiber and 6 cm × 6 cm sections of the samples from photomicrographs obtained using a transmission electron microscope with a magnification of 6500X are displayed on a CRT display of an image processing unit. FIG. 4 is a schematical representation of such an image. Next, scan lines 1~n are drawn with a pitch of 0.052 μm across the acquired image in a direction perpendicular to the axial direction of the fiber. Next, a sum of the distances of segments passing through the micropore portions within a single scan line, with the exception of the portions indicated as α, which do not comprise an entire micropore range, i.e. a1 through a5, is obtained. Subsequently, a sum total (total distance) is produced by obtaining another sum, e.g. b1 through b6, in the same manner for the second scan line, and so on until the sum of n1 through n6 is obtained for the nth line. Next a sum total of the number (total number) of the micropores through which the scan lines pass (five for the first line, six for the second line, and six for the nth line) is obtained and average distances Da, Db are obtained as total distance/total number. The microfibril length L illustrated in FIG. 2 and micrfibril spacing W can be measured in a similar manner.

[0031]

The internal diameter of the hollow fiber membrane used in the inventive aqueous condensate treatment process is preferably in the range of from 50 to 5,000 μm. If it is smaller than 50 μm, pressure losses in the hollow fiber membrane increase, which is practically inconvenient. Further, if it exceeds 5,000 μm, the surface area of the hollow fiber membrane decreases and the volume of aqueous permeate per unit volume decreases. The total membrane thickness of the hollow fiber membrane is preferably between 5 and 500 μm, and even more preferably, betwen 30 and 200 μm. If it is smaller than 5 μm, deformations may occur. Further, if it exceeds 200 µm, its water permeability decreases.

[0032]

The thickness of the dense layer is preferably 0.5 to 20 µm, and even more preferably, 3 to 12 µm. If it is smaller than 0.5 µm, pinhole defects tend to occur in the dense layer, and if it exceeds 20 µm, the volume of aqueous permeate produced by the hollow fiber membrane decreases. Further, the thickness of the dense layer is preferably not more than 1/3 of the total membrane thickness of the hollow fiber membrane. If it is thicker than that, it may be difficult to effectively obtain high water permeation performance in the hollow fiber membrane. Further, the thickness of the support layers is preferably greater than the thickness of the dense layer. The thickness of a single support layer is preferably 20 to 50 µm. If the support layers are thinner than the dense layer, sufficient membrane strength may not be obtained. Further, if it is less than 20 µm, sufficient membrane strength and aqueous permeate volume may be difficult to ensure. If it exceeds 50 µm, it may be impossible to increase the surface area of the dense layer.

[0033]

Further, the porosity of the hollow fiber membrane is preferably 75 vol% or more. Using a porosity of 75vol% or more can extend the filtration life of the membrane. Further, the maximum pore diameter of the micropores, as obtained by the bubble point method, is preferably 0.05 to 1.0 μm. The water permeation rate decreases when the maximum pore diameter is smaller than 0.05 μm and the membrane strength may decrease when it exceeds 1.0 μm.

[0034]

Polyethylene, polypropylene, poly-3-methylbuten-1, poly-4-methylbuten-1, polyvinylidene chloride, etc. are suggested as examples of the polyolefins used as the material of the hollow fiber membrane. These compounds can be used singly or as mixtures of two or more compounds.

[0035]

The MI value (melt index value) of the polyolefins, as measured in accordance with ASTM D-1238, is preferably in the range of from 0.1 to 50g/10 min, with 0.3 to 15g/10 min being even more preferable. Polyolefins whose MI value is less than 0.1g/10 min have excessively high melt viscosity, as a result of which they are difficult to mold and are not readily amenable to forming the desired microporous layers. Further, polyolefins with MI values exceeding 50g/10min, conversely, are difficult to form in a stable manner because of their excessively low melt viscosity. When polyethylene is used, the MI value, as determined by the method described in JIS K 6760, is preferably in the range of from 0.05 to 20.0g/10min, and even more preferably, in the range of from 0.1 to 5.0g/10min. If the MI value is less than 0.05g/10min, the viscosity is extremely high and melt spinning becomes more difficult. When it exceeds 20.0g/10min, the crystal orientation becomes inadequate and a uniform microporous structure cannot be obtained.

[0036]

The density of the polyolefin varies depending on its type. For instance, in case of polyethylene, a density of $0.95g/cm^3$ or more is desirable, and a density of $0.960g/cm^3$ or more is even more desirable. In case of polypropylene, a density of $0.91g/cm^3$ or more is desirable. If the density is smaller than that, the micropores formed by stretching become non-uniform and the process becomes inconvenient. These density or MI values can be freely adjusted depending on the polymerization condition settings, blends, etc. Further, the size of the micropores in each layer can be adjusted by using polyolefins with different densities and MI values as the material of the dense layer and support layers.

[0037]

A hollow fiber membrane of such a porous structure can be manufactured in the following manner. Namely, after extruding and melt-spinning molten polymer using a nozzle for hollow fiber membrane manufacture with three or more concentrically disposed annular discharge orifices at a temperature above the melting point, or, more preferably, at a temperture that is 10 to 100°C higher than the melting point of the polyolefin, the polymer is cooled at 10 to 40°C and taken up at a take-up speed of 0.1 to 3 m/sec, thereby obtaining composite unstretched hollow fiber (unstretched fiber), which is used to form the dense layer and support layers. Subsequently, stacked lamellae are formed, if necessary, by conducting heat treatment at a temperature equal to or lower than the melting point of the polyolefin or, more preferably, at a temperature that is 5 to 50°C lower than its melting point. Next, a hollow fiber membrane of a porous structure is obtained by subjecting it to stretching treatment. For the stretching treatment, it is preferable to use two-stage stretching, which is made up of cold stretching conducted at a temperature that is relatively lower, and hot stretching, which is carried out under heating.

[0038]

The cold stretching process destroys the crystalline structure of the unstretched fiber and induces uniform micro-cracking (microcracks) between the stacked lamellae. The cold stretching process is preferably conducted at a temperature between 0°C and a temperature that is 50°C lower than the melting point of the polyolefin. For example, when polyethylene is used as the polyolefin, the cold stretching temperature is between 0°C and 80°C and, more preferably, in the range of from 10°C to 50°C. Further, the cold stretch ratio is preferably between 5 and 200%. If it is less than 5%, the microcracking is not sufficient. Further, if it exceeds 200%, the stacked lamellae undergo deformation and there is a decrease in the respective porosity of the dense layer and support layers, which is undesirable.

[0039]

Hot stretching is a process, during which the micro-cracks generated by the cold stretching process are expanded and microfibrils are formed between the stacked lamellae, thereby forming a hollow fiber membrane of a microporous structure having slit-like micropores. The hot stretching temperature is as high as possible, but it should not exceed the melting point of the polyolefin. The hot stretch ratio can be appropriately selected depending on the pore diameter of the target micropores. From the standpoint of process stability, the ratio is in the range of from 50 to 2,000% and, more preferably, in the range of from 100 to 1,000%. Subsequently, in order to stabilize it dimensions, the resultant hollow fiber membrane is preferably subjected to heat setting in a constant-length or slightly relaxed state. The heat setting temperature is equal to or higher than the hot stretching temperature and does not exceed the melting temperature of the thermoplastic resin.

[0040]

Next, the hollow fiber membrane is subjected to hydrophilic treatment. Specifically, after soaking the hollow fiber membrane in a hydrophilic polymer solution obtained by dissolving a hydrophilic polymer in a solvent, a hydrophilic polymer-coated hollow fiber membrane is obtained by evarating the solvent in the course of the setting and drying treatment, to be described below.

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[0041]

A copolymer containing at least 20 mol% of ethylene and at least 10 mol% of a hydrophilic monomer is preferable as the hydrophilic polymer. This copolymer may be a random copolymer, a block copolymer, or a graft copolymer. If the content of ethylene is less than 20 mol%, the hydrophilicity of the hollow fiber membrane is weak, which is undesirable because it makes it impossible to obtain a predetermined coating rate.

[0042]

Vinyl alcohol, (meth)acrylic acid or its salts, hydroxyethyl (meth)acrylate, polyethylene glycol (meth)acrylic acid esters, vinyl pyrrolidone, acrylamide, and other vinylated compounds can be suggested as examples of the hydrophilic monomer. The compounds can be used singly or as a combination of 2 or more compounds. Among them, vinyl alcohol is the preferred compound. Further, the hydrophilic polymer may contain at least one third ingredient in addition to the ethylene and hydrophilic monomer. Vinyl acetate, (meth)acrylic acid esters, vinyl alcohol fatty acid esters, and formal [*sic; - trans.*] or butyral compounds of vinyl alcohol can be suggested as examples of the third ingredient.

[0043]

The coating rate of the hydrophilic polymer used for coating the hollow fiber membrane is in the range of from 3 to 30 wt% and, more preferably, 3 to 15 wt% per 100 wt% of the hollow fiber membrane prior to coating (hollow fiber membrane precursor). If it is less than 3 wt%, sufficient hydrophilicity cannot be obtained. If it exceeds 30 wt%, the micropores tend to become clogged by the hydrophilic polymer.

[0044]

Water-miscible organic solvents are preferred as the solvents used for the hydrophilic polymer. Methanol, ethanol, n-propanol, isopropyl alcohol and other alcohols, dimethylsulfoxide dimethylformamide, etc. can be suggested as specific examples thereof. These solvents can be used singly, but their mixtures with water are more preferable from the standpoint of providing better solubility for the hydrophilic polymer.

[0045]

Further, from the standpoint of how easy it is to obtain a solvent vapor-containing atmosphere when drying the solvent, i.e. from the standpoint of how low the solvent vapor pressure is and how toxic it is to humans, it is particularly preferable to use alcohols with a boiling point of less than 100°C, for example, methanol, ethanol, isopropyl alcohol, etc., as well as mixed solvents obtained by mixing them with water. The proportions used to mix the organic solvents with water are selected to be within ranges, within which permeation into the hollow fiber membrane is not impeded and the dissolution of the hydrophilic polymer is not decreased. Specifically, while the proportions vary depending on the type of the hydrophilic polymer, when ethanol is used, the proportion of ethanol to water is preferably in the range o from 90/10 to 30/70 (vol%).

[0046]

The concentration of the hydrophilic polymer in the hydrophilic polymer solution is in the range of from 0.1 to 10 wt% and, more preferably, from 0.5 to 5 wt%. If it is less than 0.1 wt%, it is difficult to produce a uniform coating, and if it exceeds 10 wt%, the viscosity of the solution becomes excessively high and the micropores of the hollow fiber membrane may become clogged by the hydrophilic polymer. When the hollow fiber membrane is soaked in the hydrophilic polymer solution, it is possible to soak the membrane twice or more times in a solution of the same concentration or soak it twice or more times in solutions of different concentrations. The higher the temperature of the hydrophilic polymer solution used for soaking, the lower the viscosity of the hydrophilic polymer solution and the easier it is for the hydrophilic polymer solution to penetrate through the hollow fiber membrane. However, from a safety standpoint, it is preferable for the temperature of the organic solvent to be lower than the boiling point.

The soaking time varies depending on the thickness of the hollow fiber membrane, the diameter of the micropores, and the porosity. However, the time is preferably in the range of from several seconds to several minutes.

[0047]

After soaking in the hydrophilic polymer solution, and prior to drying, it is preferable to subject the membrane to setting treatment. The purpose of the setting treatment is to prevent the micropores from being clogged by a hydrophilic polymer film, as well as adjust the rate of evaporation of the solvent in order to produce a uniform coating of hydrophilic polymer. The setting treatment is conducted by pulling up the hollow fiber membrane soaked in the soaking bath through an atmosphere comprising at least 3 vol% of an organic solvent at a temperature equal to, or higher than, room temperature and lower than the boiling point of the organic solvent, and allowing the membrane to reside in the atmosphere for at least 30 seconds.

[0048]

The surface of the hollow fiber membrane has to be prevented from rapid drying in order to prevent the formation of a hydrophilic polymer film on the surface of the hollow fiber membrane. To this end, the rate of evaporation of the solvent on the surface of the hollow fiber membrane has to be slowed down and the surface of the hollow fiber membrane has to be maintained in a moistened state. For this reason, the atmosphere used during the setting treatment is preferably an atmosphere containing solvent vapors near saturation concentration. The goal can be achieved by setting the content of the vapors of the organic solvent in the atmosphere to at least 3 vol%. In order to slow down the rate of evaporation of the solvent from the hollow fiber membrane, the temperature of the setting treatment can be set low. However, if it is set too low, this may be disadvantageous because this may prevent the removal of the solvent. For this reason, it is preferable to set the temperature of the atmosphere to a temperature equal to, or higher than, room temperature that doesn't exceed the boiling point of the solvent.

[0049]

When the hollow fiber membrane is pulled up from the soaking bath during the setting treatment, the angle, at which it is pulled up into the above-mentioned atmosphere, is preferably in the range of from 45° To 90°. When the membrane is pulled up, some of the hydrophilic polymer solution adhered to the hollow fiber membrane drips down under the action of gravity. The amount of the lost solution varies depending on the speed, at which the hollow fiber membrane is pulled up, the viscosity of the hydrophilic polymer solution, and the height, to which the hollow fiber membrane is pulled up. At such time, guides and other devices can be used to sweep the hydrophilic polymer solution off the surface of the hollow fiber membrane.

[0050]

The setting time is at least 30 seconds. If it is less than 30 seconds, the concentration of the solvent will be insufficient, the micropores might be clogged, and it may be impossible to obtain a uniform coating film. The amount of solvent that evaporates from the hollow fiber membrane when the duration of the setting treatment is set to 30 seconds is preferably between 15 and 30% of the hydrophilic polymer solution. Methods used for controlling the amount of evaporated solvent may include changing the temperature, or blowing air or inert gases at the membrane.

[0051]

Next, upon termination of the setting treatment, the hollow fiber membrane is placed in an atmosphere having a predetermined temperature and pressure, in which it is dried. Subsequently, the membrane is taken up, yielding the hollow fiber membrane coated with a hydrophilic polymer.

At such time, the feed speed of the hollow fiber membrane is preferably higher than the take-up speed in order to adjust for shrinkage, because the hollow fiber membrane undergoes shrinkage as a result of drying. If the feed speed and take-up speed are equal, the hollow fiber membrane, as a result of the shrinkage that the hollow fiber membrane undergoes, will be pulled taut and treated under a high tensile force. For this reason, the slit-like micropores will not assume an oval shape and the water permeation performance of the membrane will not be sufficiently improved. However, if the feed speed is made much faster than the take-up speed, fiber sagging may occur prior to drying and the stability of the process may suffer. For this reason, it is preferable to set the speed appropriately depending on the level of shrinkage of the hollow fiber membrane.

[0052]

Vacuum drying, hot air drying, and other publicly known drying techniques can be used for the drying treatment. The drying temperature is a temperature, at which the hollow fiber membrane is not subject to thermal deformation. For example, when the hollow fiber membrane is made of polyethylene, it is preferable to dry the membrane at a temperature of not more than 120°C and it is even more preferable to dry the membrane at a temperature of 40 to 70°C. The drying time varies depending on the average pore diameter of the micropores, the thickness of the membrane, the processing speed, etc. However, a drying time of one minute to 10 minutes should be sufficient for completely drying the hollow fiber membrane. The final coating rate of the hydrophilic polymer can be adjusted by appropriately setting the conditions of the setting and drying treatment as well as the concentration of the hydrophilic polymer solution.

[0053]

Although in the inventive process for aqueous condensate treatment, the composite microporous hollow fiber membrane may be installed in the form of a module of an arbitrary shape in any location of an aqueous condensate circulation path in order to perform aqueous condensate filtration, it is preferable to install it along a path, in which, after being heated by a heater, the condensate is supplied to a boiler. Even more preferably, aqueous condensate filtration should be performed at a point immediately prior to the water feed pump also boiler. This is effective in preventing the accumulation of cladding particles on the pump impeller blades, deposition on the feed water directing plates, deposition inside boiler tubes, etc.

[0054]

[Working Examples]

Below, the composite microporous hollow fiber membrane intended for use in hollow fiber membrane modules utilized in the inventive aqueous condensate treatment process is explained in greater detail with reference to fabrication examples. It should be noted that the various measurements and evaluations conducted in the fabrication examples were based on the following methods.

[0055]

The concentration of ethanol in the atmosphere was measured using a gas detector tube (a GasTech™ sensor tube, available from GasTec K.K.). The coating rate of the hydrophilic copolymer was calculated in accordance with the following formula (1).

[0056]

(Dry weight of hollow fiber membrane after hydrophilic treatment - Dry weight of hollow fiber membrane precursor)/Dry weight of hollow fiber membrane precursor × 100 … (1)

[0057]

The porosity of the hollow fiber membrane was determined using a mercury porosimeter Model 221 made by Carlo Erba S.A. In order to determine the volume of aqueous permeate, a mini-module with an effective membrane surface area of 70 to 90 cm^2 was fabricated and deionized water at a temperature of 25°C was filtered through the minimodule at a pressure differential of 1 kg/cm^2 (98 kPa) while measuring the volume of aqueous permeate. The cutoff particle diameter of the hollow fiber membrane was determined by filtering a liquid to be treated, which had been obtained by dispersing polystyrene latex particles of a predetermined particle size in a 0.1 wt% solution of a surface active agent (polyethylene glycol-p-isooctylphenyl ether), through a hollow fiber membrane module with a membrane surface area of about 50 cm^2 and measuring the concentration of the latex particles in the filtrate using a Hitachi spectrophotometer (U-3400) at a wavelength of 320 nm, with the particle diameter at 90% capture used as the cutoff.

[0058]

(Fabrication Example 1)

A nozzle used for hollow fiber fabrication was prepared. The nozzle had three concentrically arranged tubular discharge orifices. Molten high-density polyethylene with a density of 0.966 g/cm^3 and an MI value of 1.35 g/10min (Suntec HD-B161, manufactured by Asahi Chemical Industries Co., Ltd.), which was used for the support layers, was supplied to, and extruded from, the innermost layer and outermost layer discharge orifices and high-density polyethylene with a density of 0.960 g/cm^3 and an MI value of 0.9 g/10min (NIPOLON® HARD 5110, manufactured by Tosoh Corporation), which was used for the intermediate layer, was supplied to, and extruded from, the intermediate layer orifice of this nozzle, thereby producing melt-spun polyethylene hollow fiber with a three-layer structure. At such time the discharge temperature was set to 170°C. Further, the discharge rate of the innermost layer was set to 3.2 cc/min, the discharge rate of the outermost layer to 3.2 cc/min, and the discharge rate of the intermediate layer to 0.65 cc/min, such that the ratio of the innermost layer vs. the intermediate layer vs. the outermost layer was 4.9/1/4.9. The linear velocity of discharge was 6.1 cm/min and the draft ratio was 979.

[0059]

Next, unstretched fiber (polyethylene multilayer fiber) was obtained by taking up the fiber discharged from the nozzle at a take-up speed of 60 m/min while blowing cool air with a temperature 21°C at the fiber at an air velocity of 1 m/sec, such that the air passed around the periphery of the fiber in a uniform fashion. The resultant unstretched fiber was subjected to heat treatment for 16 hours in air heated to 115°C. Furthermore, the unstretched fiber was first subjected to a 60% cold stretch between rollers maintained at 30°C and then to a hot stretch in an oven maintained at 111°C, such that the total amount of stretch was 550%. At such time, the rate of thermal deformation was 1.3/min. After that, heat setting was carried out in an oven maintained at 120°C, yielding a composite microporous hollow fiber membrane precursor (hereinafter referred to as hollow fiber membrane precursor for short).

[0060]

Next, a hydrophilic copolymer solution was prepared by dissolving 1.0 wt% of an ethylene-vinyl alcohol copolymer with an ethylene content of 32 mol% (Soarnol DC 3203, manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) in a mixed solution of ethanol and water (mixing ratio: 60/40 vol%) that was maintained at 70°C. After soaking the obtained hollow fiber membrane precursor in this hydrophilic copolymer solution for 500 seconds, the precursor was removed from the solution and some of the excess hydrophilic copolymer solution adhered to its surface was removed. Subsequently, a hydrophilic copolymer was caused to adhere to the inner surface of the micropores of the hollow fiber membrane precursor by pulling the precursor at an angle of 90° through an atmosphere maintained at 60°C, which had an ethanol vapor concentration of 40 vol%, such that the precursor was allowed to reside in the atmosphere for 500 seconds, after which the solvent was dried with hot air at 70°C while feeding the membrane at a 10% overfeed. The coating rate of the ethylene-vinyl alcohol copolymer based on the hollow fiber membrane precursor of the resultant hydrophilized hollow fiber membrane, was 10.9 wt%. The membrane characteristics of the resultant composite microporous hollow fiber membrane (a three-layer composite membrane, in which the intermediate layer is a dense layer) are listed in Table 1.

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[0061]

(Comparative Fabrication Example 1)

A nozzle used for hollow fiber fabrication was prepared. The nozzle had two concentrically arranged tubular discharge orifices. Molten high-density polyethylene with a density of 0.960 g/cm^3 and an MI value of 0.9 g/10min (NIPOLON® HARD 5110, manufactured by Tosoh

Corporation), which was used for the support layer, was supplied to, and extruded from, the innermost layer discharge orifice and high-density polyethylene with a density of 0.966 g/cm^3 and an MI value of 1.35 g/10min (Suntec HD-B161, manufactured by Asahi Chemical Industries Co., Ltd.), which was used for the dense layer, was supplied to, and extruded from, the outermost layer orifice of this nozzle, thereby producing melt-spun polyethylene hollow fiber with a two-layer structure. At such time the discharge temperature was set to 170°C. Further, the discharge rate of the inner layer was set to 1.3 cc/min, the discharge rate of the outer layer to 10.1 cc/min, such that the discharge rate ratio of the inner layer vs. the outer layer was 1/7.7. The linear velocity of discharge was 14.3 cm/min and the draft ratio was 714.

[0062]

Next, unstretched fiber (polyethylene multilayer fiber) was obtained by taking up the fiber discharged from the nozzle at a take-up speed of 102 m/min while blowing cool air with a temperature 21°C at the fiber at an air velocity of 1 m/sec. The resultant unstretched fiber was subjected to heat treatment for 16 hours in air heated to 115°C. Furthermore, the unstretched fiber was first subjected to a 60% cold stretch between rollers maintained at 30°C and then to a hot stretch in an oven maintained at 111°C, such that the total amount of stretch was 600%. At such time, the rate of thermal deformation was 1.1/min. In addition, heat setting was carried out in an oven maintained at 120°C, thereby yielding a hollow fiber membrane precursor.

[0063]

Next, a hydrophilic copolymer solution was prepared by dissolving 1.0 wt% of an ethylene-vinyl alcohol copolymer with an ethylene content of 32 mol% (Soarnol DC 3203, manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) in a mixed solution of ethanol and water (mixing ratio: 60/40 vol%) that was maintained at 70°C. After soaking the above-mentioned hollow fiber membrane precursor in this hydrophilic copolymer solution for 500 seconds, the hollow fiber membrane precursor was removed from the solution and some of the excess hydrophilic copolymer solution adhered to its surface was removed. Subsequently, a hydrophilic copolymer was caused to adhere to the inner surface of the micropores of the hollow fiber membrane precursor by pulling the precursor at an angle of 90° through an atmosphere maintained at 60°C, which had an ethanol vapor concentration of 40 vol%, such that the precursor was allowed to reside in the atmosphere for 500 seconds, after which the solvent was dried with hot air at 70°C while feeding the membrane at a 10% overfeed. The coating rate of the ethylene-vinyl alcohol copolymer based on the hollow fiber membrane precursor of the resultant hydrophilized hollow fiber membrane, was 10.5 wt%. The membrane characteristics of the resultant composite microporous hollow fiber membrane (a two-layer composite membrane, in which the inner layer is a dense layer) are listed in Table 1.

[0064]

(Comparative Fabrication Example 2)

A nozzle used for hollow fiber fabrication was prepared. The nozzle had a single tubular discharge orifice. The molten polymer used for the intermediate layer (dense layer) in Fabrication Example 1 was extruded and melt-spun from this nozzle at a discharge rate of 2.8 g/min. At such time, the discharge temperature was set to 170°C and the membrane was taken up at a take-up speed of 35 m/min. A hydrophilized hollow fiber membrane was obtained by subjecting the resultant unstretched fiber to heat treatment, stretching, and hydrophilic treatment. The coating rate of the ethylene-vinyl alcohol copolymer based on the hollow fiber membrane precursor of the resultant hydrophilized hollow fiber membrane was 8.0 wt%. The membrane characteristics of the resultant microporous hollow fiber membrane (homogeneous membrane) are listed in Table 1.

[0065]

[Table 1]

	Outside diameter (μm)	Thickness (μm)		Porosity (%)	Volume of aqueous permeate	Cutoff particle size (μm)
		Total membrane thickness	Dense layer			
Fabrication Example 1 (membrane with dense layer as intermediate layer)						
Comparative Fabrication Example 1 (membrane with dense layer as internal layer)						
Comparative Fabrication Example 2 (homegeneous membrane)						

(*1: $L/m^2 \cdot hr \cdot kPa$ at 25°C)

[0066]

(Working Example 1 and Comparative Examples 1, 2)

Hollow fiber membrane modules of the same construction as the one illustrated in FIG. 1 described above were fabricated using the various composite microporous hollow fiber membranes and microporous hollow fiber membranes fabricated in Fabrication Example 1 and Comparative Fabrication Examples 1 and 2. A simulated aqueous condensate with a cladding (amorphous iron, 80%; α-Fe_2O_3, 20%) concentration of 100 ppb was filtered through these hollow fiber membrane modules at 40°C and an external pressure of 0.5 kg/cm^2 (49 kPa). Every week, the modules were subjected to functional recovery treatment, during which air bubble scrubbing was performed simultaneously with backwashing. The initial pressure differentials and initial aqueous permeate volumes of the hollow fiber membrane modules used in these tests, as well as their pressure differentials and aqueous permeate volumes obtained immediately after functional recovery treatment 50 days later were measured and listed in Table 2.

[0067]

[Table 2]

	Hollow fiber membrane	Volume of Aqueous Permeate (L/m^2·hr·kPa)	
		Initial	50 days later
Working Example 1	Fabrication Example 1 (membrane with dense layer as intermediate layer)		
Comparative Example 1	Comparative Fabrication Example 1 (membrane with dense layer as internal layer)		
Comparative Exmaple 2	Comparative Fabrication Example 2 (homegeneous membrane)		

[0068]

As can be seen from Table 2, the hollow fiber membrane module illustrated in Working Example 1, which utilized a three-layer hollow fiber membrane with a dense layer serving as the intermediate layer, showed excellent results in that it had a larger volume of aqueous permeate and was less prone to clogging in comparison with the composite membrane utilizing a dense layer as the internal layer (and the homogeneous membrane) of Comparative Examples 1 and 2, which exhibited the same fractionating performance.

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[0069]

[Effects of the Invention]

As described above, the hollow fiber membrane utilized in the inventive aqueous condensate treatment process is produced by laminating three or more three-dimensional membranes made of polyolefin having a plurality of micropores formed by stacked lamellae and microfibrils joined to said stacked lamellae. Its innermost layer and outermost layer serve as support layers and the intermediate layer sandwiched therebetween is a dense layer, in which the average pore diameter is smaller than that of the micropores of the support layers. For this reason, during OUT→IN filtration, more surface area can be obtained on the outside surface of the dense layer portion and the flux (water permeation performance) through the membrane can be increased in comparison with conventional hollow fiber membranes, in which the dense layer is the innermost layer. For this reason, in comparison with the conventional hollow fiber membranes, the membrane has better resistance to clogging, longer useful life and higher durability while being able to achieve a further increase in the volume of aqueous permeate. Further, during fixed flowrate filtration, the membrane offers low process pressures along with excellent backwashing restorability. As a result, it makes long-term stable operation possible and is capable of maintaining high filtration efficiency for an extended period of time. Further, during pressure filtration, the membrane exhibits excellent durability because even at considerable aqueous permeate volumes, the membrane is not prone to coalesce into a single body and the decrease in the volume of aqueous permeate over time is insignificant. Further, in comparison with the conventional hollow fiber membranes providing the same fractionating performance, the membrane offers higher volumes of aqueous permeate while retaining the same high fractionating performance aimed at complete cladding removal etc. For this reason, the amount of membrane material used can be reduced, and, as a result, the hollow fiber membrane module can be made more compact.

[0070]

Thus, the aqueous condensate treatment process utilizing such a hollow fiber membrane is capable of treating large volumes of water, provides excellent aqueous condensate purification performance with little time-dependent variation in the volume of treated water, and enables stable operation for an extended period of time and in a small footprint. Further, due to the fact that the hollow fiber membrane utilizes polyolefins, the wastes generated as a result of the aqueous condensate treatment can be incinerated and the generation of secondary wastes can be minimized.

[0071]

Further, since the above-mentioned support layers are made thicker than the dense layer and the thickness of a single support layer is set to 20-50 μm, sufficient membrane strength and aqueous permeate volumes can be ensured while increasing the surface area of the dense layer, which allows for further increasing the volume of treated aqueous condensate. Further, due to the fact that the porosity of the entire above-mentioned hollow fiber membrane is set to 75 vol%, its filtration life can be extended and, as a result, the treatment of aqueous condensates can be performed in a long-term, stable manner. Further, since the above-mentioned hollow fiber membrane is subjected to hydrophilic treatment and the microfibrils are gathered into bundles of several microfibrils each, such that the slit-like micropores are imparted an oval shape, the average pore diameter of the micropores is made larger and the volume of aqueous permeate can be increased, thereby further increasing the volume of treated aqueous condensate.

[0072]

Further, setting the rate of coating with the above-mentioned hydrophilic polymer to 3-30 wt% based on the hollow fiber membrane prior to coating makes it possible to obtain sufficient hydrophilicity and make the micropores of the hollow fiber membrane less prone to clogging, and, as a result, make ti possible to conduct aqueous condensate treatment in a long-term stable manner. In addition, setting the ratio Db/Da of the average distance Db between the microfibril bundles of the support layers to the average distance Da between the microfibril bundles of the dense layer after coating to between 1.3 and 4.0 makes it possible to obtain a hollow fiber membrane exhibiting high fractionating performance and producing large volumes of aqueous permeate. As a result, its condensate purification performance can be further enhanced and the volume of treated water can be further increased. In addition, the inventive hollow fiber membrane module for aqueous condensate treatment comprises a hollow fiber membrane produced by laminating three or more three-dimensional membranes made of polyolefin having a plurality of micropores formed by stacked lamellae and microfibrils joined to said stacked lamellae, in which the innermost layer and outermost layer serve as support layers and the intermediate layer sandwiched therebetween is a dense layer, in which the average pore diameter of the micropores is smaller than the average pore diameter of the micropores of the support layers. As a result, the membrane provides high water permeation performance and fractionating performance, is not prone to clogging, and has excellent mechanical strength and durability. Such a hollow fiber membrane is suitable for aqueous condensate treatment.

[Brief Description of the Drawings]

[FIG. 1]

A schematic cross-sectional view illustrating an exemplary hollow fiber membrane module used in the inventive aqueous condensate treatment process.

[FIG. 2]

An enlarged plan view of the layers constituting a hollow fiber membrane.

[FIG. 3]

An enlarged plan view of the layers constituting a hydrophilized hollow fiber membrane.

[FIG. 4]

A schematic view illustrating the method used for measuring the average pore diameter of the micropores.

[Description of the Reference Numerals]

3. Hollow fiber membrane.

18. Stacked lamellae.

20. Microfibrils.

21. Microfibril bundles.

22. Micropores.

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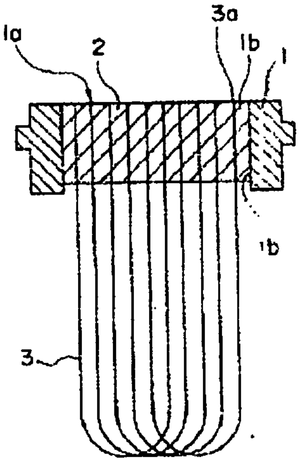
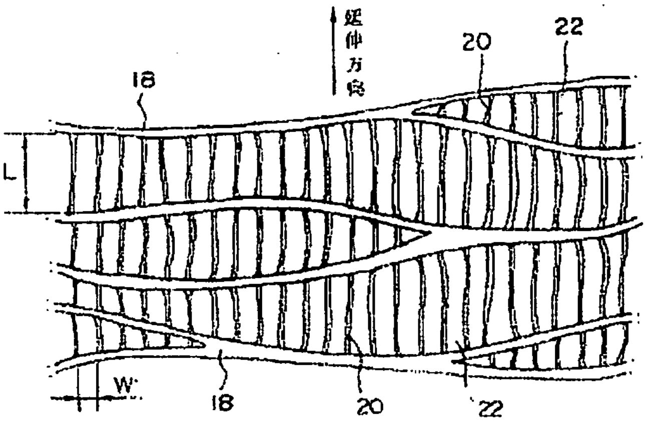
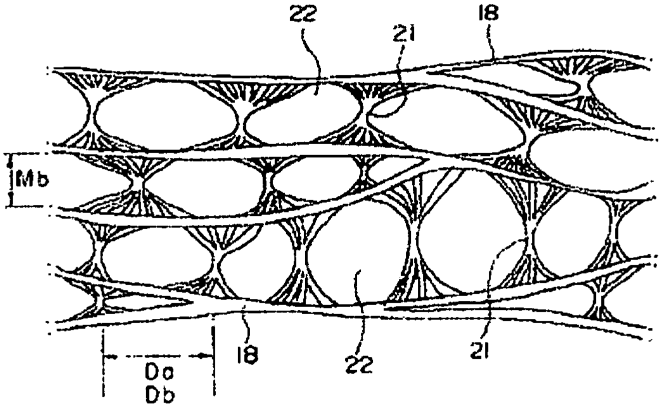
[FIG. 1]



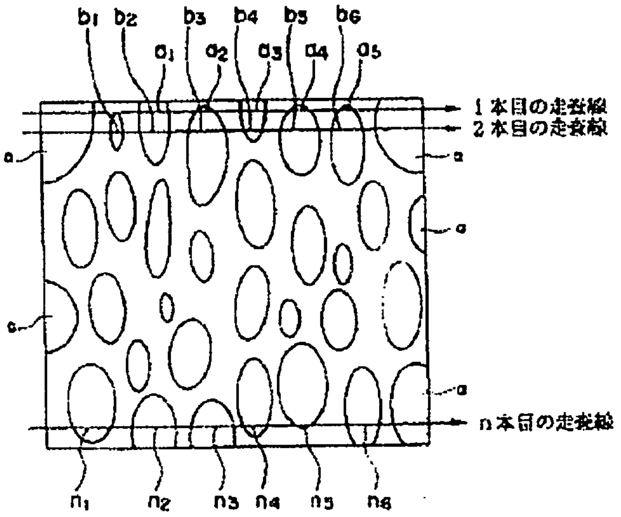
[FIG. 2]



[FIG. 3]



[FIG. 4]



//Keys, FIG. 4//

(Arrows, top to bottom) 1st scan line